

Statistical mechanics of bent twisted ribbons

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We present an analytical study of bent twisted ribbons. We first describe the elastic response of a ribbon within a purely mechanical framework. We then study the role of thermal fluctuations in modifying its elastic response. We predict the moment angle relation of bent and twisted ribbons. Such a study is expected to shed light on the role of twist in the “J factor” for DNA looping and on bending elasticity of twisted graphene ribbons.

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DNA is a twist storing polymer. Many biological processes in the cell exert torsional stresses on the DNA molecule. One would expect that such torsional stresses affect the bending elasticity of the molecule and its ability to form loops. “Cyclization” of DNA has been the focus of several studies, theoretical and experimental, *in vitro* and *in vivo*[1–4]. A proper understanding of DNA elasticity over a range of length scales is valuable to understanding biological processes. The persistence length L_P of DNA is about $50nm$. At length scales short compared to L_P the molecule is well described by a purely energetic treatment similar to that used by civil engineers to describe the twisting and bending of beams and cables[5–7]. At length scales of the order of the persistence length, the effect of thermal fluctuations becomes appreciable. The subject of this study is the role of thermal fluctuations in shaping the elastic properties of torsionally stressed macromolecular beams. Our study is general and applies equally to other systems like actin filaments or carbon nanotubes under mechanical stresses[8]. We use an approximation scheme [9–11] developed earlier to account for thermal fluctuations using the Van Vleck correction. Such an approximation works well in the stiff limit and as described earlier, works[10] suprisingly well even over length scales as large as five times the persistence length. We work within the wormlike chain model[12, 13], which views the molecule as a ribbon, carrying an energy cost for bending and twisting. The wormlike chain model has been known to describe double stranded DNA [14] as well as actin filaments[15]. Fig. 1 shows typical configurations of a twisted bent ribbon.

For clarity we consider experiments in which one end of the molecule is tethered to a glass slide, its tangent vector at the same end is constrained to lie along the \hat{t}_i direction and the molecule is torsionally constrained at both ends. We can attach a magnetic bead to the

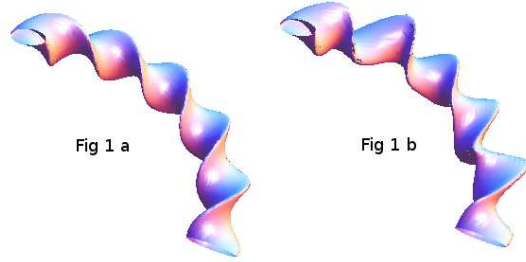


FIG. 1. Figure shows two configurations of a twisted and bent molecule with fixed end tangent vectors \hat{t}_i and \hat{t}_f . On the left (Fig. 1a) is the minimum energy configuration and on the right (Fig. 1b) the same configuration is shown slightly perturbed by thermal fluctuations.

untethered end and apply bending moments and twist up the molecule by varying the direction of an applied magnetic field. Note that we do not constrain the final position of the molecule $x(L)$ but only its final tangent vector \hat{t}_f . A uniform magnetic field will result in a pure bending moment without applying any stretching force. Plotting the bending moment vs the bending angle gives another experimental probe of the elastic properties. In this paper we derive the predictions of the wormlike chain for such experimental situations.

We present an approximate analytical solution of this statistical mechanical problem. Working with the wormlike chain model, we first write down a closed form analytical solution in parametric form, expressing the mechanical energy functional of a twisted bent ribbon as a function of the bending angle. We use this to plot the theoretically predicted moment-angle relation in the absence of thermal fluctuations. We then

compute the fluctuation determinant which describes the leading thermal correction to the energy functional. The fluctuation determinant is used to discuss the stability of the classical solutions. Finally, we describe how thermal fluctuations modify the moment angle relations and conclude with a discussion.

In the wormlike chain, we model the polymer by a ribbon, a framed space curve $\{\vec{x}(s), \hat{e}^i(s)\}$. $\vec{x}(s)$ describes the curve, $\hat{t}(s) = \frac{d\vec{x}}{ds}$, its tangent vector and $\hat{e}^i(s)$ the framing (the \hat{e}^i s are an orthonormal frame with $\hat{e}^3 = \hat{t}$). s is the arc length parameter along the curve ranging from 0 to L , the contour length of the curve. $\vec{x}(0) = 0$ since one end is fixed at the origin. The tangent vectors at both ends $\hat{t}(0), \hat{t}(L)$ are fixed to \hat{t}_i and \hat{t}_f respectively.

By simple transformations described elsewhere ([11, 16, 17]) we can reduce this problem by eliminating the twist degree of freedom. The reduced problem deals with a space curve $\vec{x}(s)$ with tangent vector $\hat{t}(s)$ subject to a writhe constraint. The energy functional is

$$\mathcal{E}(\mathcal{C}) = \frac{A}{2} \int_0^L \left(\frac{d\hat{t}}{ds} \cdot \frac{d\hat{t}}{ds} \right) ds - 2\pi\tau\mathcal{W}, \quad (1)$$

where A is an elastic constant with dimensions of energy times length. The quantity \mathcal{W} is the writhe which is constrained to take a fixed value. The constraint is enforced by the Lagrange multiplier τ , which has the physical interpretation of the torque imposed on the ribbon. (The writhe of an open space curve whose initial and final tangent vectors are fixed is defined [17] by extending the curve beyond its ends to infinity adding straight line segments with constant tangent vectors \hat{t}_i and \hat{t}_f .) We will work in the constant torque ensemble, where τ is held fixed. The quantity $L_p = A/kT$ is the persistence length. The mathematical problem we face is to compute the partition function

$$Q(\hat{t}_i, \hat{t}_f) = \sum_{\mathcal{C}} \exp \left[-\frac{\mathcal{E}(\mathcal{C})}{k_B T} \right]. \quad (2)$$

In Eq.(2), the sum is over all allowed configurations of the polymer, those which satisfy the boundary conditions for the tangent vector at the two ends: $\hat{t}_i = \hat{t}(0), \hat{t}_f = \hat{t}(L)$.

In the stiff limit, one can neglect thermal fluctuations and simply minimize the energy functional appearing in (2). The problem is formally similar to that of a symmetric top, (as was known to Kirchhoff[18]) and this greatly aids the solution. Borrowing from classical mechanics, we can use variational techniques and identify “constants of the motion” The Euler-Lagrange (E-L) equations that one arrives at from the variational prob-

lem are[17]:

$$\ddot{\hat{t}} = -\tau(\hat{t} \times \dot{\hat{t}}) + \gamma\hat{t}, \quad (3)$$

where the term $\gamma\hat{t}$ arises since $\delta\hat{t} \cdot \hat{t} = 0$. The total “energy”

$$\mathcal{H} = \frac{1}{2}(\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \quad (4)$$

is a “constant of the motion” as is the “angular momentum”

$$\vec{J} = (\hat{t} \times \dot{\hat{t}}) - \tau\hat{t}. \quad (5)$$

For positive (negative) τ , we choose the $-\hat{z}$ (\hat{z}) axis along the direction of the angular momentum \vec{J} . Below we restrict to τ positive. Similar considerations apply to negative τ with appropriate changes. We have

$$-J = J_z = \sin^2 \theta \dot{\phi} - \tau \cos \theta, \quad (6)$$

where we have introduced the usual polar coordinates on the space of tangent vectors $\hat{t} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$. Evaluating $-\hat{t} \cdot \vec{J} = \tau = J \cos \theta$ we find that the angle θ is a constant of the motion and that $\dot{\phi} = -J/\mu$. $\mu = \cos \theta$ is positive (for $\tau > 0$, a condition we assume). The solution of the Euler-Lagrange equation is $\hat{t}_{cl}(s) = (\sin \theta \cos Js, -\sin \theta \sin Js, \cos \theta)$. The tangent vector is restricted to a fixed latitude on the unit sphere (corresponding to “precession without nutation” in the top analogy). In real space the molecule describes a helix.

By choice of the x axis we set the initial and final tangent vectors to: $\hat{t}_i = (\sin \theta, 0, \cos \theta)$ and $\hat{t}_f = (\sin \theta \cos \phi_f, \sin \theta \sin \phi_f, \cos \theta)$. Considering the dot product $u = \hat{t}_i \cdot \hat{t}_f = \cos \alpha$ and setting $\mu = \cos \theta$ gives us u and therefore α as a function of μ . $u(\mu)$ is plotted in Fig. 2.

$$u(\mu) = (1 - \mu^2) \cos\left(\frac{\tau L}{\mu}\right) + \mu^2 \quad (7)$$

and an expression for α as a function of μ .

$$\alpha(\mu) = \arccos \left[(1 - \mu^2) \cos\left(\frac{\tau L}{\mu}\right) + \mu^2 \right] \quad (8)$$

For fixed α , $u = \cos \alpha$ defines a horizontal straight line (shown in black in Fig. 2), which intersects the curve (Eq. (7)) at multiple values of μ . The largest of these corresponds to the lowest value of J . The smaller values of μ correspond to higher J values and higher rates of traversal, including traversing the circle of latitude more than once. As we will see below, only the largest μ value gives a stable configuration.

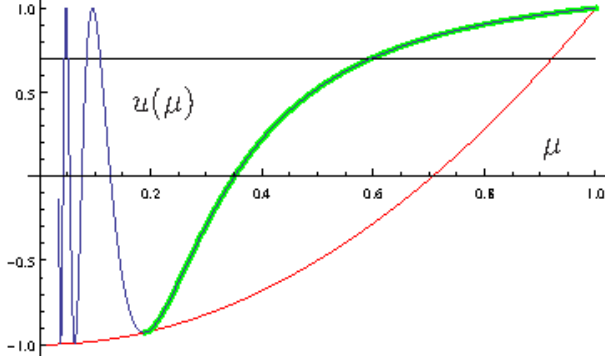


FIG. 2. A plot of $u(\mu)$ versus μ . The black horizontal line is a line of fixed α . The red parabolic line represents $2\mu^2 - 1$ which is the envelope of the curve $u(\alpha)$ near its minima. Note that the minima are very close to the points of tangency between the envelope and $u(\alpha)$.

Note that \hat{t}_{cl} remains in the northern hemisphere since $\mu > 0$. Such curves (and their small perturbations) are “good curves” [17], in the sense that they can be continuously deformed to the straight line along \hat{z} without self intersection or pointing towards $-\hat{z}$. We can therefore use Fuller’s formula for the writhe $2\pi\mathcal{W} = \int_0^L d\phi(1 - \cos\theta)$ and compute the energy functional in terms of μ by doing the integrations in (1) for the classical solution:

$$\mathcal{E}_{cl}(\mu) = \frac{\tau^2 L}{2} \left[\left(\frac{1}{\mu} + 1 \right)^2 - 4 \right] \quad (9)$$

Equations (8) and (9) give the solution $\mathcal{E}_{cl}(\alpha)$ in parametric form. Differentiating $\mathcal{E}_{cl}(\alpha)$ with respect to α gives us the moment-angle relation:

$$M_{cl}(\alpha) = \frac{\partial \mathcal{E}_{cl}}{\partial \alpha} \quad (10)$$

where the subscript cl on the left hand side of (10) reminds us that this expression ignores thermal fluctuations.

So far, we have dealt with the classical solutions of the Euler-Lagrange equations, ignoring questions of stability and thermal fluctuations. Both of these questions will now be addressed. As explained in [11] in great detail, the fluctuation determinant Δ can be calculated from the Energy functional $\mathcal{E}_{cl}(\hat{t}_i, \hat{t}_f)$ using the Van Vleck determinant

$$\Delta^{-1} = \det \frac{\partial^2 \mathcal{E}_{cl}}{\partial \hat{t}_i \partial \hat{t}_f} \quad (11)$$

This computation of this two by two determinant yields an elegant formula for the inverse of the fluctuation de-

terminant:

$$\Delta^{-1} = \frac{1}{\sin \alpha} \frac{\partial}{\partial \alpha} [M_{cl}^2(\alpha)] \quad (12)$$

where $M_{cl}(\alpha)$ the classical Moment-angle relation. Eq. (12) is the main result of this paper can be used to understand both the stability and the fluctuations around the classical solutions. Eq. (12) can be used to graphically display the free energy and moment angle relation of the ribbon.

The fluctuation determinant is the product of the eigenvalues of the fluctuation operator. A stable configuration is a local minimum of the energy and so the fluctuation operator has only positive eigenvalues. Instability sets in when at least one of the eigenvalues crosses zero. At such points the fluctuation determinant Δ vanishes. Thus, Δ Eq. (12) can be used to study the stability of classical solutions. Note first that $\mu = 1$ describe a straight line configuration. These configurations are known to be stable for $\tau < \pi/L$ [6, 17], a condition we will assume hereafter. Suppose $0 < \mu < 1$, so that $\alpha \neq 0, \pi$. At points μ_0 where $du/d\mu(\mu_0) \neq 0$, Taylor expansion reveals that $u(\mu)$, $\mathcal{E}(\mu)$ and $\alpha(\mu)$ vary linearly in $(\mu - \mu_0)$. A small calculation shows that Δ^{-1} is finite and so Δ does not vanish. It follows that configurations remain stable as long as $du/d\mu(\mu_0) \neq 0$. Instability sets in when

$$\frac{du(\mu)}{d\mu} = 0 \quad (13)$$

From Fig. 2 we see that the green region is stable but the remaining configurations are not. Eq. (13) is a transcendental equation which can be solved numerically. A glance at Fig. 2 reveals that the roots of this equation are close to (but not equal to) the points where $u(\mu)$ touches the envelope (shown in red online) $2\mu^2 - 1$, where $\alpha = 2\theta$. For a ribbon bent by angle α and subject to a torque τ , the critical line for buckling is close to $\tau = \pi/L \cos \alpha/2$, the exact value being given by the roots of Eq. (13). For torques and bending angles above the critical line the molecule buckles into a loop and cyclizes. It is evident from this formula that higher torque implies lower α for buckling. Thus torque aids cyclization as could be naively expected.

Another factor that aids cyclization is thermal fluctuations. The thermal fluctuations are easily incorporated in using Eq. (12) in the expression for the free energy

$$\mathcal{F}(\alpha(\mu)) = \mathcal{E}_{cl}(\mu) + 1/2kT \log \Delta(\mu) \quad (14)$$

This free energy can be differentiated to give the moment angle relations when thermal fluctuations are incorporated. The results are best seen in graphical form.

Fig. 3 shows the Helmholtz energy as a function of α and Fig.4 shows the Moment-Angle relations with and without thermal fluctuations.

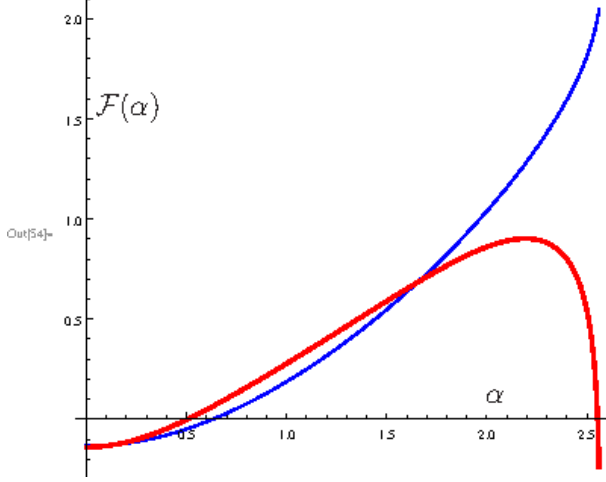


FIG. 3. The Helmholtz free energy $\mathcal{F}(\alpha)$ versus α for parameters $\tau = .3, L = 3, kT = .5$, with (thick red curve) and without thermal fluctuations (thin blue curve).

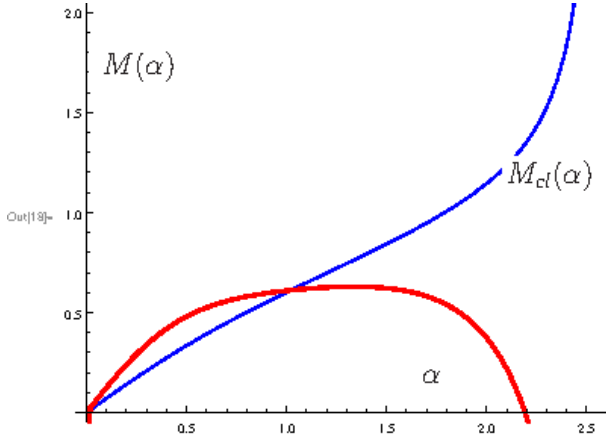


FIG. 4. Bending moment versus bending angle for the same parameter values as in Fig.3 caption ($\tau = .3, L = 3, kT = .5$). Thin blue line shows the mechanical elastic response and the thick red line includes the effect of thermal fluctuations.

To conclude, in this paper we have studied the elastic response of a bent twisted ribbon and have analyzed how thermal fluctuations modify its response. Note that the $\tau \rightarrow 0$ limit is a singular one and has to be taken with care. From $\tau = J\mu$ it follows that $\tau \rightarrow 0$ also implies $\mu \rightarrow 0$. Both τ and μ need to be taken to 0 in such a way as to keep J finite. We find that classically the energy is quadratic for small values of the bend-

ing angle and then for large bending angles it diverges. Correspondingly, the moment is initially Hookean and then diverges for large values of the bending angle.

In the presence of thermal fluctuations there is a softening of the “bending rigidity” which is reflected in the curves depicting the free energy and the moment angle relations. This has implications for cyclization and DNA looping “J factors”. Our analysis suggests that in a cellular environment, torsional stresses and thermal fluctuations enhance cyclization probability of bent polymers.

To summarize, this paper offers an analytical treatment of the mechanics and thermal fluctuations of twisted and bent polymers. We give a parametric solution of the problem, which can be used to generate plots of experimentally accessible quantities. We expect that this solvable model would be of interest to physicists and biologists interested in the cyclization of DNA.

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